DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/135,844 filed on May 24, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 12th day of October, 1999

Atsuko Ikeda

Atsuko Ikeda

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method for Producing Solid Electrolytic Capacitor

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for producing a solid electrolytic capacitor comprising a metal material having thereon a dielectric film and a solid electrolyte formed on a desired position of the dielectric film, said metal material being cut into a predetermined shape and having valve action, wherein the process of coating a solution containing a material for forming a masking member on said metal material to form a masking layer is performed twice.

[Claim 2] The method for producing a solid electrolytic capacitor comprising a metal material having thereon a dielectric film and a solid electrolyte formed on a desired position of the dielectric film, said metal material being cut into a predetermined shape and having valve action, as claimed in claim 1, wherein said method comprises:

a step of linearly coating a solution containing a material for forming a masking member around the entire circumference in the region undertaking the boundary in the application of electrochemical forming onto said metal material, and heating the solution to form a first masking layer;

a step of electrochemical forming an area where a solid electrolyte is formed later, the area being defined by the first masking layer on said metal material;

a step of further linearly coating a solution containing a material for forming a masking member around the entire circumference in the region at a predetermined distance from said first masking layer on said electrochemically formed metal material, and heating the solution to form a second masking layer;

a step of forming a solid electrolyte in the area exclusive of the space between said first masking layer and said second masking layer out of the area subjected to said electrochemical forming; and

a step of cutting said metal material in the space between said first masking layer and said second masking layer.

[Claim 3] The method for producing a solid electrolytic capacitor as claimed in claim 1 or 2, wherein said solution containing a material for forming a masking member is a low molecular weight polyimide solution or polyamic acid solution capable of being solidified by heating.

[Claim 4] The method for forming a solid electrolytic capacitor as claimed in any one of claims 1 to 3, wherein said solution containing a material for forming

a masking member further contains silicone oil, silane coupling agent or polyimidesiloxane.

[Claim 5] The method for forming a solid electrolytic capacitor as claimed in any one of claims 1 to 4, wherein said metal foil material having valve action is a metal material selected from the group consisting of aluminum, tantalum, niobium and titanium.

[Claim 6] The method for forming a solid electrolytic capacitor as claimed in any one of claims 1 to 5, wherein said solid electrolyte is a polymer solid electrolyte containing as a repeating unit a divalent group of any one of pyrrole, thiophene and aniline, or any substituted derivative thereof.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method for producing a solid electrolytic capacitor. More specifically, the present invention relates to a method for producing a solid electrolytic capacitor using a masking member in forming a solid electrolyte layer on a valve-acting metal substrate having thereon a dielectric film, in which the portion of metal substrate where the solid electrolyte layer is not provided (anode part) can be insulated without fail from the solid electrolyte layer or

an electrically conducting layer formed on the solid electrolyte layer using an electrically conducting paste or the like (cathode part).

[0002]

[Background Art]

A solid electrolytic capacitor using an electrically conducting polymer has a basic structure such that an oxide dielectric film is formed on the surface of a valve-acting metal such as aluminum, tantalum and titanium, previously subjected to etching treatment, an electrically conducting polymer which works out to solid electrolyte is formed on the oxide dielectric film, an anode lead is connected to the anode terminal (the metal surface area where the solid electrolyte is not formed) and a cathode lead is connected to the electrically conducting layer containing the electrically conducting polymer. The solid electrolytic capacitor is manufactured by finally sealing the device as a whole with insulating resins such as epoxy resins.

[0003]

Such solid electrolytes using an electrically conducting polymer for the solid electrolyte can be reduced in the equivalent series resistance and the leakage current as compared with solid electrolytic capacitors using manganese dioxide or the like for the solid electrolyte. This is advantageous in manufacturing a capacitor capable

of coping with the tendency of electronic equipments toward higher performance and smaller size. Accordingly, a large number of production methods have been proposed therefor.

In order to produce a high-performance solid electrolytic capacitor using an electrically conducting polymer, it is indispensable to secure electrical insulation of the anode part which works out to an anode terminal, from the cathode part comprising an electrically conducting layer containing an electrically conducting polymer.

[0004]

As the masking means for insulating the anode part from the cathode part of a solid electrolytic capacitor, for example, a method of coating, printing or potting epoxy resins, phenol resins or the like on an unformed area and curing the resin to prevent passing of electricity (see, JP-A-3-95910 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")), a method of electrodepositing a solution containing a polyamic salt on at least a part of the valve-acting metal in the area where the solid electrolyte is not formed, thereby forming a polyamic acid film, and dehydration-curing the film by heating to form a polyimide film (see, JP-A-5-47611), a method of forming a tape or resin coating film part made of polypropylene, polyester, silicon or

fluorine-type resin so as to prevent the solid electrolyte from climbing up (see, JP-A-5-16681), and a method of forming an insulating resin layer on the surface of a metal substrate in the boundary part between the area which works out to an anode terminal and the area where the capacitor is formed, and removing the insulating resin layer in the area other than the capacitor part to expose the metal substrate (see, JP-A-9-36003).

[0005]

The method of using phenol resins or epoxy resins as the masking material (JP-A-3-95910) is disadvantageous in that the capacitor is greatly damaged when pressed by exterior force, because the elastic modulus of resin is high and the stress against strains is high.

The method of forming a polyimide film by electrodeposition (JP-A-5-47611) may successfully form a film even inside the pore parts as compared with ordinary coating methods, however, the production cost increases because of necessity of the electrodeposition step and moreover, a dehydration step at a high temperature is necessary so as to form the polyimide film.

[0006]

The method of forming an insulating resin-made tape or resin coating film part so as to prevent the solid electrolyte from climbing up at the manufacturing (JP-A-5-

16681) has difficulty in firmly fixing the tape (film) at edge parts of the substrate and bears a risk of polymer solid electrolyte as the solid electrolyte invading the anode side.

The method of forming an insulating resin layer and then removing the insulating resin layer in the area other than the capacitor part to expose the metal substrate (JP-A-9-36003) includes a substantially useless step of once forming an insulating resin layer and then removing it.

[0007]

[Problems to be Solved by the Invention]

Accordingly, the object of the present invention is to provide a method for producing a solid electrolytic capacitor with good operability, the method comprising forming a solid electrolyte layer on a valve-acting metal substrate having thereon a dielectric film, in which a masking member is formed using a simple coating method and thereby the metal substrate area where a solid electrolyte layer is not provided (anode part) can be insulated without fail from the solid electrolyte layer or electrically conducting layer formed thereon by applying an electrically conducting paste or the like (cathode part).

[0008]

[Means to Solve the Problems]

The present inventors have made extensive

investigations on the following matters: (1) to use as a material for forming a masking member (hereinafter referred to as a masking member coating solution), for example, a solution containing a heat resistant resin or a precursor thereof, or a solution containing a low molecular weight polyimide having good insulating property and exhibiting high heat resistance after the curing or a precursor thereof; (2) to apply electrochemical forming to the cut out parts after the cutting of a metal material because in the case of conventional metal formed material foils, the cut out parts generated on the cutting into a desired dimension remain unformed and give rise to increase in the leakage current; (3) to coat the masking member coating solution using a hard and disk-like coating member having a smooth coating surface corresponding to the coating line width and at the same time coat the coating solution in a closed system so as to prevent occurrence of changes in the concentration of the masking member coating solution during the supply; and (4) to use as the solid electrolyte an electrically conducting polymer containing as a repeating unit a divalent group of any one of pyrrole, thiophene and aniline, or any substituted derivative thereof. As a result, it has been found that the object of the present invention can be attained by using in addition to the above-described matters investigated a method of treating a

metal substrate through a two-stage masking treatment, providing a solid electrolyte layer and cutting the metal substrate between two masking members, where the two-stage masking treatment is performed such that a temporary masking (first masking layer) treatment is applied before the metal substrate is cut into a predetermined dimension and then electrochemically formed, the metal substrate is electrochemically formed based on the position of the temporary masking, and a main masking (second masking layer) treatment is applied to a different portion of the substrate. The present invention has been accomplished based on this finding.

[0009]

More specifically, the present invention provides a method for producing a solid electrolytic capacitor described below:

1) a method for producing a solid electrolytic capacitor comprising a metal material having thereon a dielectric film and a solid electrolyte formed on a desired position of the dielectric film, the metal material being cut into a predetermined shape and having valve action, wherein the process of coating a solution containing a material for forming a masking member on the metal material to form a masking layer is performed twice;

2) the method for producing a solid electrolytic

capacitor comprising a metal material having thereon a dielectric film and a solid electrolyte formed on a desired position of the dielectric film, the metal material being cut into a predetermined shape and having valve action, as described in 1) above, wherein the method comprises:

a step of linearly coating a solution containing a material for forming a masking member around the entire circumference in the region undertaking the boundary in the application of electrochemical forming onto the metal material, and heating the solution to form a first masking layer;

a step of electrochemical forming an area where a solid electrolyte is formed later, the area being defined by the first masking layer on the metal material;

a step of further linearly coating a solution containing a material for forming a masking member around the entire circumference in the region at a predetermined distance from the first masking layer on the electrochemically formed metal material, and heating the solution to form a second masking layer;

a step of forming a solid electrolyte in the area exclusive of the space between the first masking layer and the second masking layer out of the area subjected to the electrochemical forming; and

a step of cutting the metal material in the space

between the first masking layer and the second masking layer;

3) the method for producing a solid electrolytic capacitor as described in 1) or 2) above, wherein the solution containing a material for forming a masking member is a low molecular weight polyimide solution or polyamic acid solution capable of being solidified by heating;

4) the method for forming a solid electrolytic capacitor as described in any one of 1) to 3) above, wherein the solution containing a material for forming a masking member further contains silicone oil, silane coupling agent or polyimidesiloxane;

5) the method for forming a solid electrolytic capacitor as described in any one of 1) to 4) above, wherein the metal foil material having valve action is a metal material selected from the group consisting of aluminum, tantalum, niobium and titanium; and

6) the method for forming a solid electrolytic capacitor as described in any one of 1) to 5) above, wherein the solid electrolyte is a polymer solid electrolyte containing as a repeating unit a divalent group of any one of pyrrole, thiophene and aniline, or any substituted derivative thereof.

[0010]

Figs. 1(a) to 1(f) show the outline of the production

steps of a solid electrolytic capacitor according to the present invention. Fig. 1(a) is a plan view of a metal material (1) having thereon a porous oxide film, which is cut into a predetermined size and works out to a substrate of a solid electrolytic capacitor. Fig. 1(b) is a plan view showing the state where the first masking layer (2) is applied. Fig. 1(c) is a plan view showing the state where a electrochemically formed layer (3) is provided so as to form a porous oxide film without fail on the cut end parts produced accompanying the cutting. Fig. 1(d) is a plan view showing the state where a second masking layer (4) is applied. Fig. 1(e) is a plan view showing the state where a solid electrolyte (5) is formed. Fig. 1(f) is a plan view of a solid electrolytic capacitor device (10) resulting from cutting of the metal substrate between the first masking layer (2) and the second masking layer (4). Fig. 2 shows a cross section of the solid electrolytic capacitor (10). As seen in Fig. 2, a lead wire (7) is connected to the anode terminal (6) assumed by the cutting plane, a lead wire (8) is connected to the cathode assumed by the solid electrolyte layer (5) or an electrically conducting layer (not shown) formed thereon using an electrically conducting paste or the like, and the whole is sealed with an insulating resin (9) such as epoxy resins, thereby completing the solid electrolytic capacitor.

[0011]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

[Valve-Acting Metal]

The substrate of the solid electrolytic capacitor is a valve-acting metal having on the surface thereof an oxide dielectric film. The valve-acting metal is selected from aluminum, tantalum, niobium, titanium, a valve-acting metal foil or bar of an alloy system using aluminum, tantalum, niobium or titanium as a matrix, and a sintered body mainly comprising such a metal material. The metal has a dielectric film on the surface thereof due to oxidation by oxygen in air. However, in order to ensure the formation of dielectric oxide film, the metal is preferably subjected to etching or the like in advance by a known method to roughen the surface and then electrochemically formed in a usual manner. The valve-acting metal is preferably an aluminum foil having thereon an aluminum oxide layer.

The valve-acting metal after the surface roughening treatment is preferably cut into a size agreeing with the shape of the solid electrolytic capacitor, before use.

The thickness of the valve-acting metal foil varies depending on the use purpose, however, it is generally from 40 to 150 μm. The size and the shape of the valve-acting metal foil also vary depending on the use, however, the

metal foil as a plate-form device unit preferably has a rectangular shape having a width of from 1 to 15 mm, more preferably from 2 to 5 mm, and a length of from 1 to 15 mm, more preferably from 2 to 6 mm.

[0012]

[Electrochemical Forming]

The valve-acting metal cut into a predetermined shape is electrochemically formed by various methods. By previously performing electrochemical forming, increase of the leakage current can be prevented even if defects are generated in the second masking layer.

The conditions for electrochemical forming are not particularly limited. For example, the electrochemical forming is performed using an electrolytic solution containing at least one of oxalic acid, adipic acid, boric acid, phosphoric acid and the like under the conditions such that the concentration of electrolytic solution is from 0.05 to 20 wt%, the temperature is from 0 to 90°C, the current density is from 0.1 to 200 mA/cm^2, the voltage is a numerical value selected according to the electrochemical forming voltage of a film already present on the formed foil to be treated, and the electrochemical forming time is 60 minutes or less. More preferably, the conditions are selected in the range such that the concentration of electrolytic solution is from 0.1 to 15 wt%, the

temperature is from 20 to 70°C, the current density is from 1 to 100 mA/cm^2 and the electrochemical forming time is 30 minutes or less.

The above-described conditions for electrochemical forming are suitably used in industry, however, as long as the oxide dielectric film already formed on the surface of the valve-acting metal material is not ruptured or deteriorated, various conditions such as kind of electrolytic solution, concentration of electrolytic solution, temperature, current density, electrochemical forming time and the like, may be freely selected.

If desired, the metal material may be subjected before or after the electrochemical forming to a treatment such as dipping in phosphoric acid for improving the water resistance, and heating or dipping in boiling water for strengthening the film.

[0013]

[Masking Member]

The first masking is provided so as to prevent the electrochemical forming solution from running out to the portion which works out to anode of a solid electrolytic capacitor. Accordingly, for the first masking member, a composition comprising heat-resistant resins in general, preferably heat-resistant resins or precursors thereof soluble in or swellable with a solvent, and further

containing inorganic fine particle and cellulose-based resins (see JP-A-11-80596) may be used, but the material is not limited. Specific examples thereof include polyphenylsulfones (PPS), polyethersulfones (PES), cyanic ester resins, fluororesins (e.g., tetrafluoroethylene, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers), low molecular weight polyimides and derivatives thereof. Among these, low molecular weight polyimides, polyether sulfones, fluororesins and precursors thereof are preferred.

For the second masking, the same material for the first masking member may be used. In particular, polyimides are preferred because of its sufficiently high adhesive strength to the valve-acting metal, good filling property, capability of withstanding a heat treatment up to 450°C and excellent insulating property.

[0014]

Polyimides are conventionally used as a solution prepared by dissolving a polyamic acid as a precursor in a solvent and after the coating, the solution is imidized by a heat treatment at a high temperature. Thus, a heat treatment at from 250 to 350°C is necessary and this causes a problem such as rupture of the dielectric layer on the surface of anode foil due to the heat.

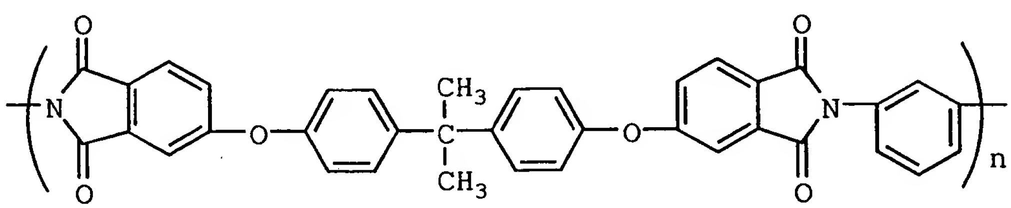
Polyimides used in the present invention are satisfactorily curable by a heat treatment at a low

temperature of 200°C or less, preferably from 100 to 200°C, and reduced in the external shocks such as rupture or breakage of the dielectric layer on the surface of anode foil.

The polyimides are a compound containing an imide structure in the main chain. Examples of the polyimides which can be preferably used in the present invention include the compounds represented by the following formulae (1) to (4) each having a flexible structure where intramolecular rotation readily takes place in the diamine component skeleton, and polyimides represented by the following formula (5) obtained by the polycondensation reaction of 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride with aromatic diamines. The polyimides preferably have an average molecular weight of from 1,000 to 1,000,000, more preferably from 2,000 to 200,000.

[0015]

[Chem. 1]

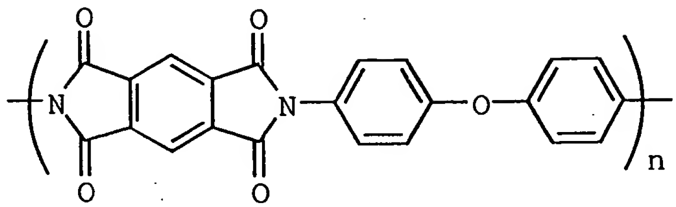


(1)

(ULTEM, produced by General Electric Co.)

[0016]

[Chem. 2]

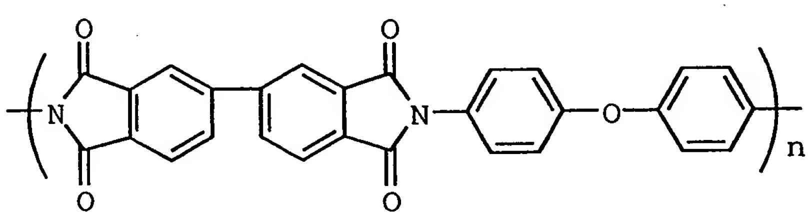


(2)

(VESPEL SP, produced by E.I. du Pont de Nemours & Co.)

[0017]

[Chem. 3]

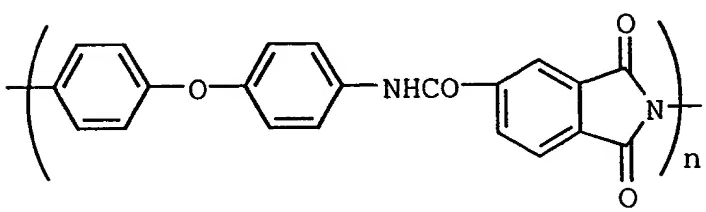


(3)

(UPIMOL R, produced by Ube Industries, Ltd.)

[0018]

[Chem. 4]

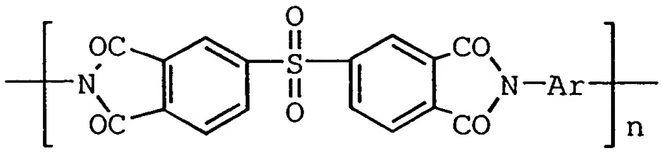


(4)

(TORLON, produced by Amoco Chemicals Corp.)

[0019]

[Chem. 5]



(5)

(DSDA polyimide)

[0020]

These compounds each can be dissolved or dispersed in organic solvents, therefore, a solution or dispersion solution having a solid concentration (in turn viscosity) suitable for the coating operation can be easily prepared. The concentration is preferably from 10 to 60 wt%, more preferably from 15 to 40 wt%. The viscosity is preferably from 50 to 30,000 cp, more preferably from 500 to 15,000 cp. If the concentration or viscosity is less than this range, the masking line may be blurred, whereas if the concentration or viscosity exceeds the range, cobwebbing or the like occurs and an unstable line width results.

[0021]

Specific examples of the polyimide solution which can be preferably used include a solution obtained by dissolving low molecular polyimides curable by a heat treatment after the coating, in a solvent reduced in the hygroscopicity such as 2-methoxyethyl ether and triethylene glycol dimethyl ether (the solution is commercially

available, for example, under the trade name of "UPICOAT FS-100L" from Ube Industries, Ltd.), and a solution obtained by dissolving polyimide resins represented by formula (5) in NMP (N-methyl-2-pyrrolidone) or DMAc (dimethylacetamide) (the solution is commercially available, for example, under the trade name of "Rikacoat" from Shin Nippon Rika K.K.).

[0022]

In the former case, the solution coated is thermally modified into a polymer and cured by a heat treatment at from 160 to 180°C, as a result, a flexible film having high heat resistance and good insulating property is formed. The polyimide film obtained maintains rubber-like properties such that the tensile strength is 2.0 kg/mm^2, the elongation of cured film is 65% and the initial elastic modulus is 40.6 kg/mm^2, and at the same time exhibits high heat resistance such that the thermal decomposition temperature is 461°C. Furthermore, the volume resistivity is as high as 10^{16} Ω•cm even under humidification and the dielectric constant is as low as 3.2, thus the polyimide film holds excellent electrical properties as the insulating film.

In the latter case, a film excellent in the heat resistance, mechanical properties, electrical properties and resistance against chemicals can be formed merely by

removing the solvent at a temperature of 200°C or less. The film obtained has a tensile strength of about 11.8 kg/mm^2, a cured film elongation of 14.2%, an initial elastic modulus of 274 kg/mm or more and a heat resistance such that the temperature for weight reduction of 5% is 515°C. The volume resistivity is 10^{16} Ω•cm and the dielectric constant is 3.1 (25°C) or 2.8 (200°C), thus, the film holds excellent electrical properties.

[0023]

In the present invention, the masking member solution may contain a defoaming agent (e.g., lower alcohol type, mineral oil type, silicone resins type, oleic acid, polypropylene glycol), a thixotropy-imparting agent (e.g., silica fine powder, mica, talc, calcium carbonate) or a silicon agent for resin modification (e.g., silane coupling agent, silicone oil, silicon-based surfactant, silicone-based synthetic lubricant). For example, by adding a silicone oil (e.g., polysiloxane) and a silane coupling agent, improvements may be expected in the defoaming property (to prevent bubbling at curing), releasability (to prevent adhering of electrically conducting polymer), lubricity (permeability inside the pore part), electrical insulating property (to prevent leakage current), water repellency (to prevent climbing up of the solution at the polymerization of electrically conducting polymer), damping

and vibrationproofing property (to oppose pressure at the stacking of capacitor device), or heat resistance and weatherability of resin (introduction of crosslinking mechanism).

In the present invention, the above-described effects by virtue of addition of silicone oil (polysiloxane) may also be similarly obtained by using a composition comprising soluble polyimidesiloxane and epoxy resin (see, JP-A-8-253677).

[0024]

[Coating Method of Masking Member]

Fig. 3(a) (plan view) and Fig. 3(b) (side view) show an outline of one example of the apparatus used for coating the masking member.

The apparatus of Fig. 3 is constructed to complete 1 cycle consisting of supply of the masking member solution, coating of the masking member on a substrate and cleaning of the masking member remaining on the roll surface, during 1 rotation of the disk-like coating member (11).

In the figure, 15 is a metal-made guide for fixing one end of a plurality of valve-acting metal material substrates (1a, 1b, 1c ...) for a solid electrolytic capacitor like long strips are fixed.

In the circumferential periphery of the disk-like coating member (11), means (12) for supplying the masking

member solution to the coating surface is disposed at the rear of the contacting position with the substrate (backward in the rotating direction), and a scraper (13) and a wiping off member (14) both for cleaning the coating surface of the rotating roll are disposed in front of the contacting position with the substrate (1).

[0025]

In this apparatus, the means (12) for supplying the masking member solution supplies the masking member coating solution to the coating member in a closed system so as to prevent occurrence of changes in the concentration of the masking member coating solution during the supply. More specifically, the coating solution is stored in a closed container, supplied to the coating surface using a non-pulsating pump through a tube member, and coated by sending the masking member to the surface and edges of a metal material while pressing the coating surface of the disk to a desired portion of the plurality of metal material substrates (1a, 1b, ..., 1z) held on the metal-made guide (15) under the control of the moving (feeding) rate of the guide (15) and the rotating speed of the disk. Thereafter, the masking member solution is similarly coated on the opposite surface, thus accomplishing uniform coating over the entire circumference. It is also possible to coat the masking member at once on the front and back surfaces and

both edges of a substrate using two units of disk-like coating members.

[0026]

[Solid Electrolyte]

In the present invention, the solid electrolyte is preferably an electrically conducting polymer containing as a repeating unit a divalent group of any one of pyrrole, thiophene and aniline structures, or any substituted derivative thereof. However, those conventionally known as the material for the solid electrolyte may be used without any particular limitation.

For example, a method of coating a 3,4-ethylenedioxythiophene monomer and an oxidizing agent each preferably in the form of a solution separately one after another or simultaneously on the oxide film of metal foil (see, JP-A-2-15611 and JP-A-10-32145) may be used.

In general, aryl sulfonate-type dopants are used in the electrically conducting polymer. Examples of the salt which can be used include salts of benzenesulfonic acid, toluenesulfonic acid, naphthalenesulfonic acid, anthacenesulfonic acid and anthraquinonesulfonic acid.

[0027]

[Examples]

The present invention is described below by referring to Examples, however, the present invention should not be

construed as being limited to the following Examples.

[0028]

Example 1:

First Masking Step

A 100 μm-thick formed aluminum foil cut (slit) into a width of 3 mm was cut into strips each having a length of 13 mm. One short side part of a foil strip was fixed to a metal-made guide by welding. A polyimide resin solution (Rikacoat, produced by Shin Nippon Rika K.K.) adjusted to a viscosity of 800 cp was supplied to a disk-like coating apparatus having a 0.4 mm-width coating surface and while press-contacting the coating surface of the coating apparatus onto the aluminum formed foil, a 0.8 mm-width line was drawn by the solution on the portion 7 mm inside from the unfixed end. The solution was then dried at about 180°C to form a first masking layer (polyimide film).

[0029]

Electrochemical Forming Step

The aluminum foil fixed to a metal-made guide was disengaged from the coating apparatus. Thereafter, the area from the distal end to the first masking line of the aluminum foil was dipped in an aqueous ammonium adipate solution and a voltage of 13 V was applied to electrochemically form the unformed area on the cut end portion. Thus, a dielectric film was formed.

[0030]

Second Masking Step

The aluminum foil fixed to a metal-made guide was again mounted on the coating apparatus and a 0.8 mm-width line was drawn by the polyimide resin solution (RIKACOAT, produced by Shin Nippon Rika K.K.) on the portion 4 mm inside from the unfixed distal end in the same manner as above. The solution was dried at about 180°C to form a second masking layer (polyimide film).

[0031]

Solid Electrolyte Forming Step

In the electrochemically formed layer region exclusive of the space between the first masking layer and the second masking layer, a solid electrolyte was formed as follows. More specifically, the area (3 mm × 4 mm) opposite to the first masking layer side with respect to the second masking layer formed 4 mm inside from the distal end of aluminum foil was dipped in an isopropanol solution containing 20 wt% of 3,4-ethylenedioxythiohene (Solution 1), pulled up and left standing at 25°C for 5 minutes. Thereafter, the aluminum foil area treated with the monomer solution was dipped in an aqueous solution containing 30 wt% of aqueous ammonium sulfate solution (Solution 2) and then dried at 60°C for 10 minutes to allow oxidative polymerization to proceed. The operation from dipping in

Solution 1 to oxidative polymerization by dipping in Solution 2 was repeated 25 times to form a solid electrolyte layer.

[0032]

Cutting Step

The thus-prepared aluminum foil element having formed thereon a solid electrolyte layer was subjected to coating of carbon paste and silver paste in the area where the electrically conducting polymer layer was formed, thereafter, the aluminum foil was cut off between the first masking layer and the second masking layer.

[0033]

Fabrication and Test of Chip-Type Solid Electrolytic Capacitor Device

Three sheets of cut foil in the moiety having the second masking layer were superposed by joining one on another with silver paste, an anode lead terminal was welded to the portion free of the electrically conducting polymer, the whole was sealed with epoxy resin, and the device obtained was aged at 120°C for 2 hours while applying a rated voltage. In this manner, 30 units in total of chip-type solid electrolytic capacitors were manufactured. Fig. 4 shows a cross section of the thus-manufactured chip-type solid electrolytic capacitor.

These capacitor devices were subjected to a reflow

soldering test by passing each device through a temperature zone at 230°C for 30 seconds. The leakage current 1 minute after the application of a rated voltage was measured and an average leakage current of devices having a measured value of 1 CV or less was determined. When the leakage current was 0.04 CV or more, the device was determined as defective. The results obtained are shown in Table 1.

[0034]

Example 2:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Example 1 except for using a polyimide resin solution (UPICOAT FS-100L, produced by Ube Industries, Ltd.) as the first masking member. The measurement of leakage current and the reflow soldering test were also performed in the same manner. The results obtained are shown in Table 1.

[0035]

Example 3:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Example 1 except for using a polyimide resin solution (UPICOAT FS-100L, produced by Ube Industries, Ltd.) as the first and second masking members. The measurement of leakage current and the reflow soldering test were also performed in the same manner. The results obtained are shown in Table 1.

[0036]

Example 4:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Example 3 except that the oxidative polymerization in the step of forming a solid electrolyte was performed by dipping the aluminum foil in an aqueous solution prepared by further adding sodium 2-anthraquinonesulfonate (produced by Tokyo Chemical Industry Co.) to Solution 2 to have a concentration of 0.07 wt%. The measurement of leakage current and the reflow soldering test were also performed in the same manner. The results obtained are shown in Table 1.

[0037]

Example 5:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Example 3 except that the oxidative polymerization in the step of forming a solid electrolyte was performed by dipping the aluminum foil in an aqueous solution prepared by further adding sodium 2-naphthalenesulfonate (produced by Tokyo Chemical Industry Co.) to Solution 2 to have a concentration of 0.06 wt%. The measurement of leakage current and the reflow soldering test were also performed in the same manner. The results obtained are shown in Table 1.

[0038]

Comparative Example 1:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Example 1 except that masking was performed once. More specifically, the chip-type solid electrolytic capacitor was manufactured by forming a polymer (polyimide) film only through the second masking step (masking at the site of 4 mm inside from the distal end of the aluminum foil) and then subjecting the aluminum foil to electrochemical forming, formation of solid electrolyte and cutting off. The measurement of leakage current and the reflow soldering test were performed in the same manner. The results obtained are shown in Table 1.

[0039]

Comparative Example 2:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Comparative Example 1 except that a tape comprising a heat resistant substrate and a heat resistant pressure sensitive adhesive was bonded in the width of 1 mm to the front and back surfaces of the aluminum foil in place of forming the second masking layer. The measurement of leakage current and the reflow soldering test were performed in the same manner. The results obtained are shown in Table 1.

[0040]

Comparative Example 3:

Chip-type solid electrolytic capacitors were manufactured in the same manner as in Comparative Example 1 except that a 0.8 mm-width line was drawn on the front and back surfaces of the foil by coating and curing phenol resin in place of forming a polymer insulating film. The measurement of leakage current and the reflow soldering test were performed in the same manner. The results obtained are shown in Table 1.

[0041]

[Table 1]

	Average Leakage Current	Heat Resistance Failure Ratio in Reflow Soldering Test
Example 1	0.20 μA	0/30
Example 2	0.19 μA	0/30
Example 3	0.17 μA	0/30
Example 4	0.16 μA	0/30
Example 5	0.16 μA	0/30
Comparative Example 1	0.32 μA	1/30
Comparative Example 2	2.0 μA	4/30
Comparative Example 3	2.2 μA	5/30

[0042]

[Effects of the Invention]

The method for producing a solid electrolytic capacitor of the present invention is advantageous in the following points as compared with conventional techniques.

(a) Since polyimide resins are used as a masking member in place of conventionally used tape or epoxy or phenol-type resins, the electrically conducting polymer-impregnated part and the anode part can be completely separated, the leakage current can be in turn reduced, and the stress generated at the reflow treatment or the like during or after the formation of a capacitor device can be relaxed.

(b) Since the cut end part of the formed foil in the moiety which is to be masked later is electrochemically formed in a perfect manner, the increase of leakage current due to invasion of electrically conducting polymer or electrically conducting paste into the cut end part can be prevented.

[0043]

(c) By virtue of the first masking (temporary masking), the electrochemically forming solution is prevented from running out over the masking at the subsequent electrochemically forming step and a necessary area (area exclusive of the anode part of the solid

electrolytic capacitor) can be electrochemically formed with ease and no fail. More specifically, if the temporary masking is not present, the electrochemically forming solution may run out over the substrate and the leakage current at the electrochemical forming becomes large to cause short circuit to the electrode. The occurrence of short circuit may be reduced by taking a space between the position of electrochemically forming solution and the position of electrode using a long substrate (metal foil), however, decrease in the profitability and the productivity results.

Furthermore, in the case of not providing a temporary masking, the amount of the electrochemically forming solution run out is difficult to control and the electrochemically formed state cannot be controlled. According to the two-stage masking method of the present invention, these problems can be solved.

[0044]

(d) The polyimide film used as a masking member has resistance against water-based solvents or organic solvents such as alcohols, used at the polymerization of the electrically conducting polymer, therefore, the insulation between the anode part and the cathode part can be maintained without fail.

[BRIEF DESCRIPTION OF DRAWINGS]

[Fig. 1]

Figs. 1(a) to 1(f) each is a view showing the outline of the production step of a solid electrolytic capacitor according to the present invention.

[Fig. 2]

Fig. 2 is a cross section of an example of the solid electrolytic capacitor device.

[Fig. 3]

Fig. 3(a) is a plan view and Fig. 3(b) is a side view each showing the outline of the coating apparatus.

[Fig. 4]

Fig. 4 is a cross section of the solid electrolytic device manufactured in Examples.

[Description of Numerical References]

1 valve-acting metal (metal material having thereon a porous oxide film)

2 first masking layer

3 electrochemically formed layer

4 second masking layer

5 solid electrolyte layer

6 anode terminal

7 anode lead

8 cathode lead

9 sealing resin

10 solid electrolytic capacitor device

11 disk-form coating member

12 means for supplying masking member solution

13 scraper

14 wiping off member

15 metal-made guide

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method for producing a solid electrolytic capacitor, in which the insulation between the anode part and the cathode part can be ensured without fail fundamentally by providing masking members using a simple coating method.

[MEANS TO SOLVE THE PROBLEM]

A method for producing a solid electrolytic capacitor, comprising a step of linearly coating a solution containing a material for forming a masking member in the region undertaking the boundary in the application of electrochemical forming onto a valve-acting metal material and heating the solution to form a first masking layer; a step of electrochemically forming an area where a solid electrolyte is formed later; a step of forming a second masking layer at a predetermined distance from the first masking layer; a step of forming a solid electrolyte in the area exclusive of the space between the first masking layer and the second masking layer out of the area subjected to the electrochemical forming; and a step of cutting the metal material in the space between the first masking layer and the second masking layer.

[SELECTED DRAWING] Fig. 1